On The Cu-Pd Phase Diagram

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The Cu-Pd phase diagram has been examined by several investigators employing various experimental techniques [34Tay, 39Jon, 55Sch, 71Sou, 86Bro, 90Hua]. Subramanian and Laughlin [91Sub] have critically evaluated the Cu-Pd phase diagram based on all data available through 1985. The phase diagram evaluated by Hansen [58Han] (which was reproduced in [86Mas]) shows an order-disorder transformation involving the fcc and the $L1_2$ phase at Pd concentrations less than about 19 at.%, whereas the structure of the low-temperature ordered phase at higher Pd content (up to about 27 at.%) is tetragonal. At still higher Pd content (about 40 at.%), the disordered fcc phase transforms into an ordered phase with the $B2$ structure. Jaumot and Sawatzky [56Jau] identified a eutectoid reaction, $\alpha \rightarrow L1_2 + B2$ at about 400 °C. Based on their X-ray diffraction study, Soutter *et al.* [71Sou] proposed a phase diagram showing two peritectoid reactions. In a theoretical study of the stability of long-period superstructures (LPS) and the application of the ANNNI (axial next-nearest neighbor Ising) model to the Cu-Pd system, de Fontaine *et al.* [85Fon] also have suggested the existence of these peritectoid reactions.

Numerous studies on phase transformations in almost the entire range of Cu-Pd alloys have clearly established the existence of the disordered fcc, the $L1_2$, the 1-D LPS, the 2-D LPS, and the $B2$ phases [39Jon, 55Sch, 57Hir, 71Sou, 76Guy]. Several high-resolution electron microscopy (HREM) studies have been carried out on the LPS that form in these alloys [81Ter, 82Guy, 86Bro, 88Tak], and the existence of polytypes with the structure <3>, <4>, <8>, *etc.* have been established clearly [82Guy, 86Bro, 88Tak]. Here, the notation introduced by [80Fis] in which <*n*> represents LPS with an antiphase shift after every *n* unit cells of $L1_2$, has been adopted. It may be mentioned that some studies [67Che, 68Myl, 70Sat] have indicated that a clustering tendency exists in Pd-rich Cu-Pd fcc alloys.

In this note, we present the Cu-rich portion of the Cu-Pd phase diagram determined during a recent transmission electron microscopy (TEM) study on phase transformations in Cu-Pd al-

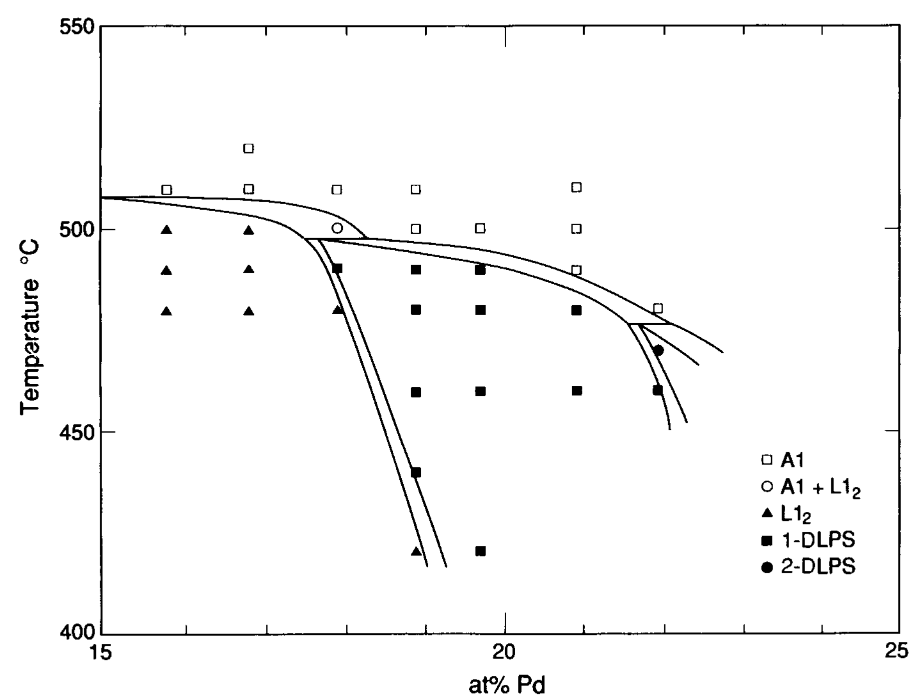

Fig. 1 Experimentally determined Cu-rich portion of the Cu-Pd phase diagram.

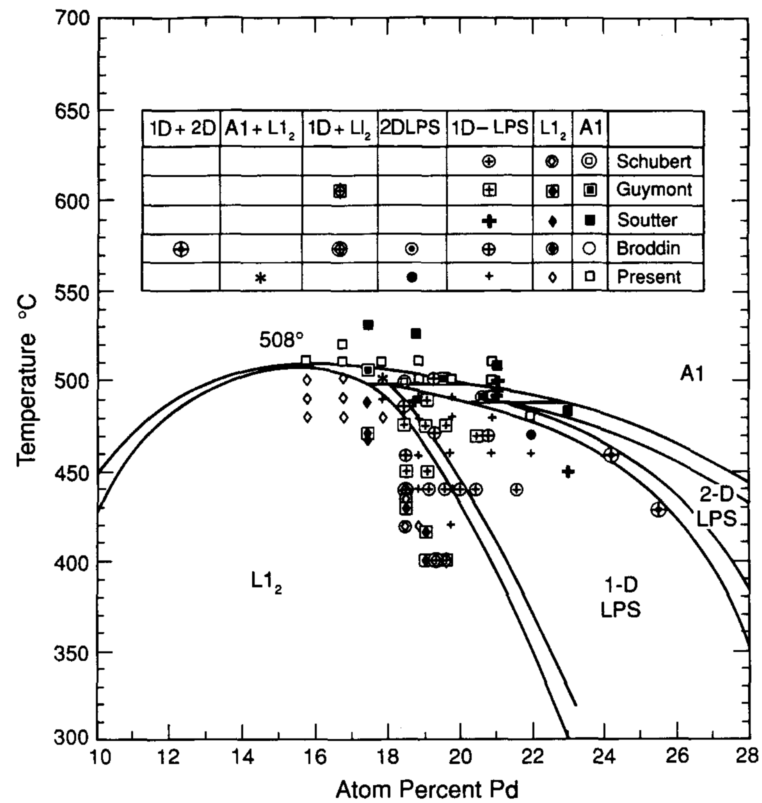

Fig. 2 Cu-Pd phase diagram from 10 to 28 at.% Pd with selected data.

loys [90Hua]. Equilibrium microstructures were produced by heat treating homogenized Cu-Pd alloys containing 15.8, 16.8, 17.9, 18.9, 19.7, 20.9, and 21.9 at.% Pd at various temperatures in the range 400 to 520 °C for periods extending up to 10 days. The alloy compositions were determined by energy dispersive X-ray spectroscopy (EDS) to an accuracy of ±0.2 at.%, and the heat treatment temperatures were controlled to within ±1 °C. Various phase fields were identified by selected area diffraction (SAD) and also by phase contrast imaging in a JEOL 200CX HREM. Great care was exercised while interpreting the data, because an SAD from a sample containing two variants of the 1-D LPS and the $L1_2$ phase could easily be confused with that containing all three vaiants of the 1-D LPS, *etc.*

The Cu-rich portion of the phase diagram as determined from this study is shown in Fig. 1. The 1-D LPS forms through the peritectoid reaction $\alpha + L1_2 \rightarrow \alpha_1$ at 495 °C and the 2-D LPS through the peritectoid reaction, $\alpha + \alpha_1 \rightarrow \alpha_2$ at 475 °C. It may be pointed out that all the two-phase fields in this region of the phase diagram are extremely narrow. In Fig. 2, all the available experimental phase diagram data are collected, and the phase boundaries evaluated by Subramanian and Laughlin [91Sub] have been incorporated. A careful examination shows that the disordering temperatures determined by all the workers except that of Soutter *et al.* [71Sou] are in good agreement and is slightly below that inferred by Subramanian and Laughlin, shown in a comparison of Fig. 1 and 2.

The present experimental data suggest the peritectoid reaction involving the 2-D LPS to be about 10 °C lower than that estimated by Subramanian and Laughlin. In general, the phase boundaries as deduced from the present work are in good agreement with most of the published experimental data. Figure 3 shows the phase boundaries evaluated by Subramanian and Laughlin, including the *B*2 phase field. Present data have also been included.

An important point that may be mentioned here is that the phase region denoted as the 1-D LPS actually represents a large number of single-phase fields of long-period superstructures separated by narrow two-phase regions, where each single-phase field corresponds to a long-period superstructure with a characteristic modulation period. This follows from HREM observations of polytypes such as <8>, <65>, <4>, *etc.* in various Cu-Pd alloys [82Guy, 86Bro, 88Bro, 88Tak, 90Hua]. Theoretical studies [90Ced] also have predicted various polytypes that exist in equilibrium depending on composition and temperature. A detailed discussion of this study may be found in a recent study of phase transformation in Cu-Pd alloys [90Hua].

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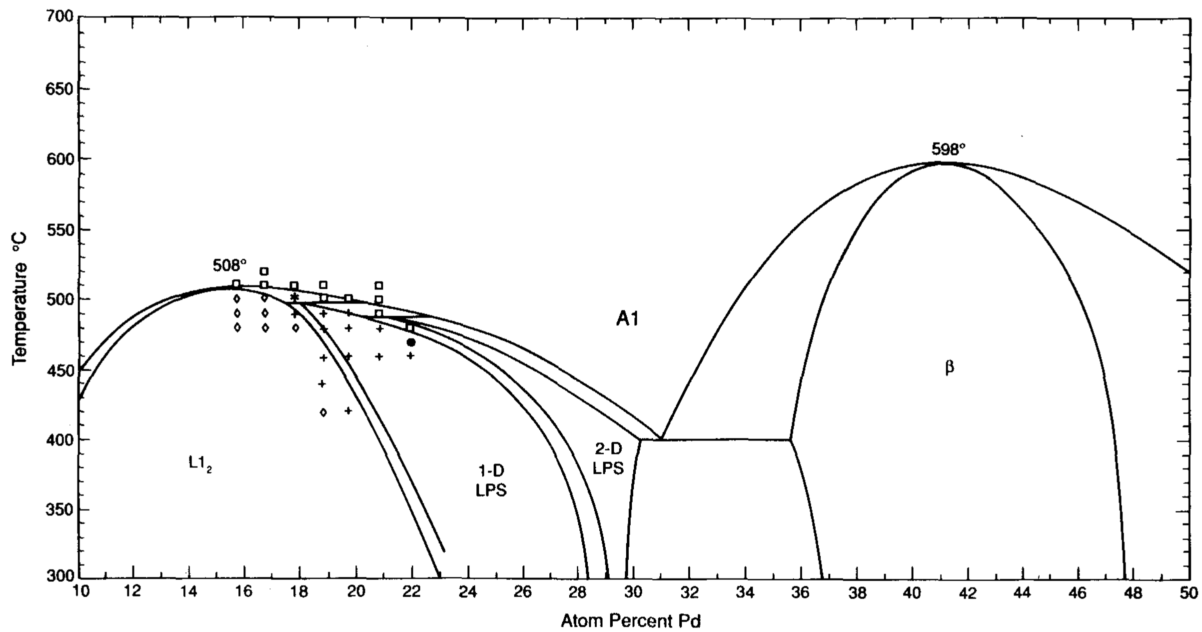

Fig. 3 Phase boundaries according to [91Sub] and present experimental data.

Cited References

34Tay: R. Taylor, "Transformations in the Copper-Palladium Alloys," *J. Inst. Met., 54,* 255-272 (1934).

39Jon: F.W. Jones and C. Sykes, "The Transformations in the Copper-Palladium Alloys," *J. Inst. Met., 65,* 419-433 (1939).

55Sch: K. Schubert, B. Kiefer, M. Wilkens, and R. Haufler, "On Some Metallic Ordered Phases with Long Periods," *Z. Metallkd., 46,* 692-715 (1955).

56Jau: F.E. Jaumot and A. Sawatzky, "Order-Disorder and Cold-Work Phenomena in Cu-Pd Alloys," *Acta Metall., 4,* 127-144 (1956).

57Hir: M. Hirabayashi and S. Ogawa, "On the Superstructure of the Ordered Alloy Cu_3Pd. II. X-ray Diffraction Study," *J. Phys. Soc. Jpn., 12*(3), 259-271 (1957).

58Han: M. Hansen and K. Anderko, *Constitution on Binary Alloys,* McGraw-Hill, New York, 612 (1958).

67Che: T. Chen, "Effect of Local Atomic Order on Magnetic Properties of Cu-Pd Alloys," Ph.D. Dissertation, Univ. Minnesota (1967).

68Myl: K.M. Myles and J.B. Darby, Jr., "Thermodynamic Properties of Solid Pd-Cu and Pt-Cu Alloys," *Acta Metall., 16,* 485-492 (1968).

70Sat: Y. Sato, J.M. Silvertsen, and L.E. Toth, "Low Temperature Specific Heat Study of Cu-Pd Alloy," *Phys. Rev. B, 1*(4), 1402-1410 (1970).

71Sou: A. Soutter, A. Colson, and J. Hertz, "Crystallographic Analysis of the Long-Range-Order Phases and of the Mono-Periodic and Bi-Periodic Antiphase Structures in Binary Cu-Pd Alloys," *Mém. Sci. Rev. Metall., 68*(9), 575-593 (1971).

76Guy: M. Guymont and D. Gratias, "On the Stability of Periodically Antiphased Alloys," *Phys. Status Solidi, 36,* 329-334 (1982).

80Fis: M.E. Fisher and W. Selke, *Phys Rev. Lett., 44,* 1502-1505 (1980).

81Ter: O. Terasaki and D. Watanabe, "Two-Dimensional Antiphase Structures of 2d-Cu_3Pd Type Studied by High Voltage, High Resolution Electron Microscopy," *Jpn. J. Appl. Phys., 20*(6), L381-L384 (1981).

82Guy: M. Guymont, R. Portier, and D. Gratias, "Incommensurate Statistical Structures Among Long Period Ordered Alloys," *Int. Phys. Conf. Ser., 61,* 387-390 (1982).

85Fon: D. de Fontaine, A. Finel, S. Takeda, and J. Kulik, "Application of the ANNNI Model to Long-Period Superstructures in Some Noble Metal Alloys," Proc. TMS-AIME Symposium on Phase Diagram, Alloy Phase Stability and Thermodynamic Aspects of Noble Metal Alloys, New York 110 (1985).

86Bro: D. Broddin, G. Van Tendeloo, J. Van Landuyt, S. Amelinckx, R. Potier, M. Guymont, and A. Loiseau, "Long-Period Superstructures in Cu_3Pd," *Philos. Mag. A, 54,* 395-416 (1986).

86Mas: T.B. Massalski, J.L. Murray, L.H. Bennett, and H. Baker, *Binary Alloy Phase Diagrams,* American Society for Metals, Metals Park, OH, 947-948 (1986).

88Bro: D. Broddin, G. Van Tendeloo, J. Van Landuyt, S. Amelinckx, and A. Loiseau, "Chaotic and Uniform Regimes in Incommensurate Antiphase Boundary Modulated Cu_3Pd Alloys," *Philos. Mag. B, 57,* 31-48 (1988).

88Tak: S. Takeda, J. Kulik, and D. de Fontaine, "One-Dimensional Long-Period Superstructures in Cu_3Pd Observed by High Resolution Electron Microscopy," *J. Phys. F, Met. Phys., 18,* 1387-1404 (1988).

90Ced: G. Ceder, D. de Fontaine, H. Dreysse, D.M. Nicholson, G.M. Stocks, and B.L. Gyorffy, "*Ab Initio* Study of the Cu-Pd One-Dimensional Long-Period Superstructure Phase Diagram," *Acta Metall., 38,* 2299-2308 (1990).

90Hua: P. Huang, S. Menon, and D. de Fontaine, unpublished research (1990).

91Sub: P. Subramanian and D. Laughlin, *J. Phase Equilibria,* to be published (1991).